

Potential of Lignosulphonate of Eucalyptus Lignin from Pulp Plant as Dispersant in Gypsum Paste

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Abstract

Eucalyptus lignin was isolated from kraft black liquor through acidification by using H₂SO₄. To effectively utilize black liquor waste from pulp plant, lignin was converted into sulphonated hydroxymethylated phenolized sulphuric acid lignin compound (SHP-SAL), which is soluble in water. SHP-SAL was obtained through the sequence of (1) phenolation of sulphuric acid lignin (SAL) into phenolized sulphuric acid lignin (P-SAL), (2) hydroxymethylation of P-SAL into hydroxymethylated phenolized sulphuric acid lignin (HP-SAL), and (3) sulphonation of HP-SAL into SHP-SAL. The derived lignin of SHP-SAL characterized by infrared spectrometry showed a significant absorption at 630 cm⁻¹, which indicates the presence of S–O bond, and absorption at 1118 and 1059 cm⁻¹, which are characteristics of C–O bonds in lignosulphonates. Assessment of SHP-SAL as a dispersant in gypsum paste was done according to C230-90 ASTM standard. The synthesized SHP-SAL has approximately 60% higher dispersability than those of commercial sodium lignosulphonate (comm. SLS) and commercial calcium lignosulphonate (comm. CLS). It is equal to the dispersability of sulphonated naphthalene formaldehyde (SNF), one of the high-performing sulphonate compounds.

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1. Introduction

Black liquor is wasted cooking liquid obtained from chemically pulp processing. This liquid has high lignin content 12-46%. Lignins are complex phenolic polymers occurring in higher plant tissues and are the second most abundant terrestrial polymer after cellulose. Due to their very complex structure, lignins are amorphous polymers with rather limited industrial use [1]. In general, black liquor processing in pulp

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industries is done to reutilize cooking chemical compound contained in it. In addition, all organic compounds in the black liquor are utilized as fuel to generate steam for manufacturing process and electricity generator. Factors limiting lignin utilization include its chemical structure and solubility characteristics. Lignin is not soluble in water, acid solution, and hydrocarbon solution. It is soluble only in light alkaline and a few organic compounds such as dimethylformide and tetrahydrofuran [2-3].

Initially, liginosulphonate and other lignin-based products were considered as industrial wastes with limited utilization. The advancement in lignin technology has induced certain product development that can compete with other expensive synthetic materials. Modification or chemical conversion of lignin is generally done to strengthen the dispersion, complexity, or bonding properties of final products. The added value of liginosulphonate products is the fact that essentially they are not toxic, of renewable natural resources origin, and environmentally safe. Environmental concern has put a focus on the utilization of additives from plant origin such as water soluble liginosulphonate [4]. For the last three decades, main components used in additives have been water soluble petrochemical-based polymers and synthetic polymers including sulphonated naphthalene formaldehyde (SNF) and sulphonated melamine formaldehyde (SMF). However, SNF is made from non-renewable materials, it has production limitation, and it is not easy to be degraded whereas SMF has toxic properties [5].

Liginosulphonate is an anionic surfactant with certain surface activity level that can improve surface adsorption and particle dispersion. The use of liginosulphonate as an additive material varies including as a dispersant in various particle dispersion systems (such as gypsum paste and cement paste) and pesticide formulas, emulsifier and dispersant for recovery process in oil drilling industries, color dispersant in textile industries, paint and ink, binding material in ceramic and urea, and emulsifier for asphalt and lubricant. This study is aimed at improving the benefits of eucalyptus lignin contained in black liquor of pulp plant into SHP-SAL, Figure 1, as a dispersant for gypsum paste preparation.

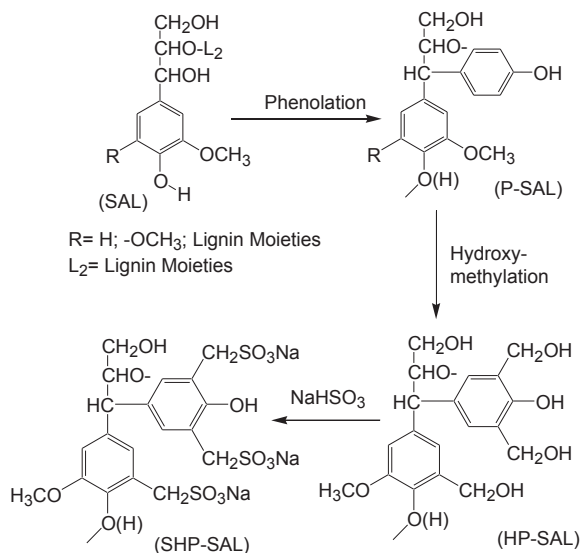


Fig. 1. Conversion of eucalyptus lignin into sulphonated hydroxymethylated phenolized sulphuric acid lignin (SHP-SAL)

2. Experiment

2.1. Materials

Black liquor was obtained from PT Toba Pulp Lestari, North Sumatra, Indonesia, which was produced from eucalyptus wood in kraft processing. Sodium lignosulphonate (SLS) used as a reference chemicals was obtained from Aldrich. Commercial SLS (comm.SLS), commercial calcium lignosulphonate (comm. CLS), and sulphonated naphthalene formaldehyde (SNF) were purchased from PT FOSROC Indonesia, and gypsum powder was obtained from ordinary building material shop.

2.2. Isolation of sulphuric acid lignin (SAL) from black liquor [6]

Black liquor was filtered and 200 mL of the filtrate was put into an Erlenmeyer flask and precipitated gradually by adding of 20% H₂SO₄ until pH 2, as monitored by an Inolab WTW pH meter. The precipitated lignin was separated from the acidified black liquor by centrifugation. Lignin purity was improved by redilution of the precipitate in NaOH 1 N. The precipitate was then filtered by using filter paper resulting in lignin solution with higher purity level than the original. This lignin solution is precipitated further by gradually adding of 20% H₂SO₄ until pH 2 is obtained (similar to the first precipitation process). Lignin was washed with H₂SO₄ 0.01 N and distilled water, and dried in an oven at 60 °C.

2.3. Phenolation of sulfuric acid lignin (SAL) [7]

A mixture of 1.0 g of SAL and 6.3 g of phenol in 15 mL of 72% sulfuric acid was stirred at 60 °C for 6 h. After quenching by dilution with 560 mL of water, the suspension was boiled for 3 h. The solids were filtered out and were thoroughly washed with warm water to give 1.2 g of phenolized SAL (P-SAL). The molecular weight of P-SAL per C₉–C₆ unit was estimated to be 275.

2.4. Hydroxymethylation of P-SAL [8]

To a solution of P-SAL in 1 or 2 M of NaOH was added by 37% formalin and the solution was stirred at 60 °C for 4 h. After acidification with HCl 1 M, the hydroxymethylated product (HP-SAL) was separated by centrifugation. The number of introduced hydroxymethyl groups was calculated according to the assumption that all of the weight gain of the reaction product is attributed to the hydroxymethyl group.

2.5. Neutral sulfonation of HP-SAL [9]

A 400 mg sample of HP-SAL and 40 mL of sulfite solution (pH 8) in a small stainless steel pressure tube was heated under various conditions. The reaction mixture was dialyzed with a cellulose tube, which had a 3500 molecular weight cutoff, to remove inorganic reagents. The reaction products were lyophilized to yield water-soluble polymer (SHP-SAL).

2.6. Determination of sulfur and sodium in SHP-SAL [10]

0.500 g SHP-SAL was put into a digestion flask, added with 5 mL HNO₃ p.a. and 0.5 mL HClO₄ p.a. and leaves the solution for a night. The following day, the solution was heated in a digestion block at 100

°C for an hour before the temperature was raised to 150 °C. The digestion temperature was further raised to 200 °C after a yellow color vanished. The destruction completed as white smoke emerged to leave an extract of about 0.5 mL. The flask was lifted and left to cool. The extract was diluted with deionized water until the volume reaches 50 mL, stirred to homogenized. The extract was used for sodium and sulfur determinations.

2.7. SHP-SAL characterization by FTIR spectrophotometry

1 mg SHP-SAL was mixed with 300 mg KBr, pulverized, pelletized, and analyzed further by a Tensor 37 FTIR Bruker spectrophotometer.

2.8. Assessment of lignosulphonate as dispersant in gypsum paste

The study consisted of two parts. The first part was the assessment of lignosulphonate compound of 0.05-0.2% (w/w) as dispersant in gypsum paste preparation. The second part was the assessment of lignosulphonate performance as dispersant in comparison with commercial lignosulphonates (SNF, commercial SLS, commercial CLS).

2.9. Assessment of the effects of lignosulphonate level as dispersant on gypsum paste (ASTM C230-90) [11]

Samples of SHP-SAL, commercial SLS, and Aldrich SLS were prepared in the level of 0.05, 0.1, 0.15, and 0.2% (sample weight/gypsum powder weight). The 88 mL water of 20 °C was mixed with the samples. Then, 110 g gypsum powder was added into sample solution and stirred for 15 sec. The mixture was poured into a ring-shaped container with a diameter of 50 mm and height of 50 mm before it was put on a flattish glass plate. The ring was then lifted up for 10 sec to let gypsum paste spread over the glass plate.

Dispersion performance was determined by calculating % flow value by using a small-scaled assessment device. Final diameter, ϕ_{final} , was measured and % flow value was determined by using the following formula:

$$\%Flow\ value = \frac{\phi_{final} - \phi_{in}}{\phi_{in}} \times 100 \quad (1)$$

Where ϕ_{final} is final diameter and ϕ_{in} is initial diameter (50 mm).

2.10. Assessment of lignosulphonate performance as dispersant

To determine the performance of SHP-SAL as dispersant, reference compounds including Aldrich SLS, commercial SLS, commercial CLS, and SNF were used. Each sample was prepared at the level of 0.1% (sample weight/gypsum weight). Compound preparation and assessment were similar to those used in the assessment of level effects. As a blank, gypsum without any sample inclusion was used. The percentage of flow value was then calculated.

3. Results and Discussion

3.1. Conversion of lignin into SHP-SAL

Low hydrophilicity property of lignin has made modification or conversion of lignin from its chemical structure necessary. This can be done by sulphonating lignin into a lignosulphonate salt. The performance of lignosulphonate as dispersant is affected by its structure, sulphur content, and the molecular weight. Dispersibility of lignosulphonate increases as its sulphonate content and molecular weight increases [8]. Sulphonate group is easy to substitute benzylic carbon in lignin unit. However, there is only one benzylic carbon in lignin component unit. One way to improve sulphonation degree of sulphuric acid lignin (SAL) is by the addition of a reactive compound such as hydroxymethylphenolic group into SAL structure. This can be initiated by reacting SAL and phenol to form phenolized sulphuric acid lignin (P-SAL) to improve lignin sulphonation degree and reactivity. Then, P-SAL is reacted with formaldehyde (HCHO) to form hydroxymethylated phenolized sulphuric acid lignin (HP-SAL). The increasing benzylic –OH group in HP-SAL makes it possible to add more sulphonate groups to the sulphonation process of HP-SAL into SHP-SAL [3].

The SAL phenolation reaction is aimed at adding phenolic group into and substituting benzylic–OH in SAL to form phenolic SAL (P-SAL). In SAL phenolation reaction, it is assumed that there is one *p*-hydroxyphenyl bonded per unit of phenylpropane of SAL. Thereafter, P-SAL is reacted with formalin to form hydroxymethylated phenolized-SAL (HP-SAL). It was suspected that in P-SAL hydroxymethylation reaction hydroxymethyl groups (–CH₂OH) substitute all aromatic H atoms with *ortho* position toward phenolic –OH. Theoretically, activating property of phenolic –OH groups makes hydroxy methylation degree maximum when the three *ortho* H atoms are substituted by –CH₂OH groups, which are easier to reach. In this study, it is estimated that P-SAL hydroxymethyl reaction results in maximum hydroxymethylation degree. The increasing number of benzylic –OH groups in the HP-SAL makes more sulphonate groups available to be added in the sulphonation process. The formation of sulphonated hydroxymethylated phenolized sulphuric acid lignin (SHP-SAL) is expected to improve its performance as dispersant. This is in agreement with Matsushita and Yasuda [8] which found that the dispersability of lignosulphonate is affected by the number of sulphonate groups added.

SHP-SAL compound obtained in this study is completely water soluble. It has Na and S contents of 21.0 % and 18.4 %, respectively. The higher Na and S contents in SHP-SAL compound than those in SLS of Wesco Technology standard [12], which are 7 % and 6.6 %, respectively, Table 1, indicates that SHP-SAL contains sulphonate groups with higher Na and S, and hence, higher sulphonation.

Table 1. Sulphonated hydroxymethylated phenolized sulphuric acid lignin (SHP-SAL) characteristics compared to Wesco Technology sodium lignosulphonatete (SLS)

Characteristic	SHP-SAL	Wesco Technology SLS
Water solubility	soluble	soluble
Na (%)	21	7
S (%)	18.4	6.6

3.2. Characteristics of SHP-SAL Function Group

In order to assess the success of lignin conversion into SHP-SAL, a FTIR analysis of P-SAL, HP-SAL, and SHP-SAL was conducted. Figure 2 shows FTIR spectra of sulphuric acid lignin (SAL), phenolized sulphuric acid lignin (P-SAL), hydroxymethylated phenolized sulphuric acid lignin (HP-

SAL), and sulphonated hydroxymethylated phenolized sulphuric acid lignin (SHP-SAL). It can be seen that the FTIR spectra of the four compounds differ. In 1600–500 cm^{-1} , different spectrum of SAL and P-SAL are seen. Higher adsorption intensity at 833 cm^{-1} in P-SAL than at 835 cm^{-1} in SAL indicates the existence of aromatic substituent in *para* position. This also indicates the formation of P-SAL as the result of SAL phenolation. In HP-SAL spectrum, differences in P-SAL spectra before and after hydroxymethylation are observed. In P-SAL, an absorption band in 2932 cm^{-1} , for stretching of methyl and methylene C-H groups, is observed. However, in HP-SAL more absorptions are observed at 2933, 2831, 2779, and 2715 cm^{-1} , for the stretching of methyl and methylene C-H. An absorption is also observed at 773 cm^{-1} , which is identified as substituted aromatic C-H groups in *ortho* position. This indicates that hydroxymethylation groups in *ortho* position are already formed.

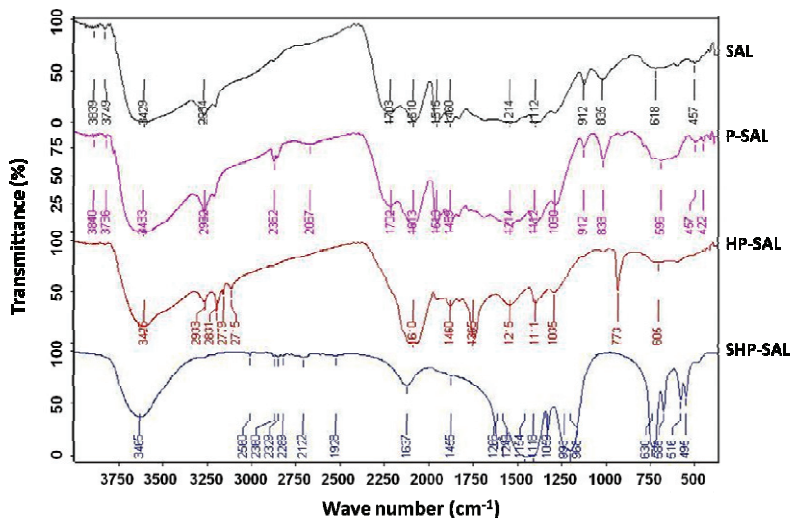


Fig. 2. FTIR Spectrums of SAL (a black line), P-SAL (a purple line), HP-SAL (a red line), and SHP-SAL (a blue line)

SHP-SAL formation can be seen from differences in HP-SAL and SHP-SAL spectra, namely HP-SAL before and sulphonated SHP-SAL, Figure 2. In SHP-SAL spectra, there is a sharp absorption at 630 cm^{-1} , which is an S-O group resulted from sodium bisulfite reaction substituting aliphatic -OH groups [13]. Absorption is also observed at 1118 and 1059 cm^{-1} which is a characteristic of C-O group in lignosulphonate [14]. S-O and C-O absorptions at these wavenumbers are not observed in FTIR PH-SAL spectra. These results show that sulphonation reaction of HP-SAL into SHP-SAL takes place.

3.2. Effects of Lignosulphonate as Dispersant in Gypsum Paste Preparation

Gypsum fluidity has a relation with dispersant content and dispersability is assessed by % flow value [15-16]. In this study, SHP-SAL compound was assessed as a dispersant in gypsum paste and the result was compared with commercial sodium lignosulphonate (SLS) and Aldrich SLS. The assessment of the effects of lignosulphonate (0.05–0.2% w/w) was done to obtain its optimum level as dispersant in gypsum. The relation between % flow value and SHP-SAL, commercial SLS, Aldrich SLS is given in Figure 3.

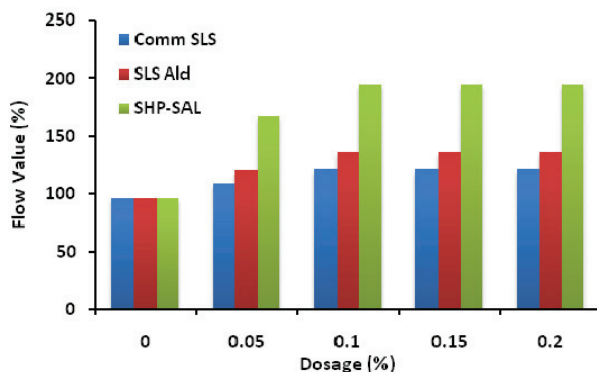


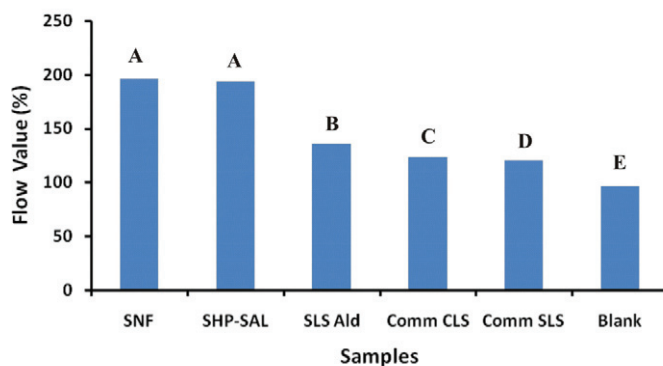
Fig. 3. Percent flow value of commercial sodium lignosulfonate (Comm. SLS), SLS Aldrich, and sulphonated hydroxymethylated phenolized sulphuric acid lignin (SHP-SAL)

Percent flow value measured without any additive as a blank is 96.4. In general, the addition of each sample compound into gypsum shows an increase in % flow value and the highest increase is found in SHP-SAL addition. For the three compounds, % flow value begins to increase at the addition of 0.05% level and it keeps increasing until 0.1% level. Meanwhile, at 0.15% and 0.20% level, % flow value increase is not significant. At the addition of 0.05% SHP-SAL into gypsum paste, % flow value increases to 166.2% and it keeps increasing up to 194.4% at 0.1% level. The addition level from 0.05% to 0.1% in commercial SLS and Aldrich SLS resulted in % flow values of 116.2-130.3% and 120.2-136.2%, respectively, Figure 3. These results are in accordance with those reported by Lee *et al.* who obtained the maximum % flow value at the level of 0.1% of SNF addition and of 0-0.35% commercial lignosulphonate addition into gypsum paste. This is due to the establishment of optimum condition, i.e. an even distribution of dispersant constituent in the gypsum [17].

3.4. Dispersibility of sample compounds

The comparison of % flow value of six samples including SHP-SAL compound, Aldrich SLS, commercial SLS, commercial CLS, SNF, and blank is shown in Figure 4. SNF is an additive material that exhibits the best dispersibility. SHP-SAL has a flow value of 194.36% and those of SNF, Aldrich SLS, commercial CLS, and commercial SLS are 196.2, 130.3, 124.1, and 120.4%, respectively (Figure 4). These results show that the synthesized SHP-SAL has dispersibility of 61.5-56.6%, which are higher than those of commercial SLS and commercial CLS, and relatively similar to % flow value of SNF. The results of Tukey test show that SHP-SAL performance is equal to that of SNF but it is different from or even better than the other controls. SNF is found to have the the best dispersibility as the additive material.

The results of dispersibility assessment of lignosulphonate found in this study are in accordance with those of Matsushita and Yasuda, who reported that the performance of lignosulphonate as dispersant is affected by (1) higher SHP-SAL molecular weight so that it has a bigger spatial centrifugal force, and (2) higher sulphonate content resulting in a higher electrostatic repulsion force. Lignosulphate dispersability increases as sulphonate sulphuric acid content and molecular weight increase. Matsushita & Yasuda [8] found that SHP-SAL sulphonate has a higher, about 30-70%, dispersability than that of commercial lignosulphonates. This might be caused by higher SHP-SAL molecular weight resulting in higher steric resistance and higher sulphuric content resulting in higher electrostatic repulsion [8].



Note: Same script indicates no difference based on Tukey test

Fig. 4. Percentage of flow value at the rate of 0.1% (w/w)

4. Conclusion

Sulphonated hydroxymethylated phenolized sulphuric acid lignin (SHP-SAL) synthesized from conversion of eucalyptus lignin gives satisfying results as a dispersant in gypsum paste. Dispersability of SHP-SAL in gypsum paste shows better performance than those of commercial SLS and commercial CLS. SHP-SAL has 61.5–56.6% higher dispersability than those of commercial SLS and commercial CLS and the same % flow value as that of SNF. Although the dispersability is not significantly different, Tukey test results show that SHP-SAL tends to have higher performance than those of control specimens.

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